NOTES

THE REACTION OF SODIUM METAPERIODATE WITH SOME NITROGEN DERIVATIVES OF CARBOHYDRATES

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Methods which might be used in the chemical degradation of carbon-14-labelled carbohydrates required an investigation of the reaction of sodium metaperiodate with certain nitrogen-containing carbohydrate derivatives. The aim of these experiments was to convert specific carbon atoms of the carbohydrates to formic acid, which could then be oxidized to carbon dioxide with mercuric acetate. The carbon dioxide was then converted to barium carbonate and its activity determined.

The oxidation of phenylosazones (1) and phenylosotriazoles (2) by sodium metaperiodate resulted in the rapid consumption of the theoretical quantity of metaperiodate. This was followed, in the case of the phenylosazones, by a slow overoxidation by the metaperiodate. Recently the metaperiodate oxidation of some phenylhydrazones has been reported by O'Donnel and Percival (3), who found that the consumption of oxidant corresponded to the amount required for an acyclic structure. They did not determine the quantities of formaldehyde and formic acid produced during the oxidation.

D-Mannose phenylhydrazone and D-xylose 2,4-dinitro-phenylhydrazone have been oxidized with sodium metaperiodate in aqueous ethanol; the metaperiodate consumed, the formic acid and formaldehyde produced were then measured.

The experimental and theoretical results, for an acyclic structure are shown in Table I (mole/mole).

TA	BL	Æ	[
			-

	Theoretical			Experimental		
	104	НСНО	нсоон	104	НСНО	нсоон
D-Mannose phenylhydrazone D-Xylose 2,4-dinitro-phenylhydrazone	4.00 3.00	$\begin{array}{c} 1.00\ 1.00 \end{array}$	$\begin{array}{c}3.00\\2.00\end{array}$	$\begin{array}{c} 4.05\\ 3.02 \end{array}$	$\begin{array}{c}1.05\\1.01\end{array}$	2.96 2.06

These phenylhydrazones probably exist in solution as cyclic structures. On oxidation they form unstable intermediates which break down further.

The metaperiodate uptake and the formic acid released were determined using the procedure quoted by Hough (1). The formaldehyde was determined by the method of Perry and Pietak (4). The experimental results show that both of the compounds are oxidized in the open chain form by metaperiodate.

The metaperiodate oxidation of two other nitrogen derivatives was studied; these were 6-O-toluene-p-sulphonyl-(tosyl)-D-glucose phenylosotriazole and 6-O-benzoyl-D-glucose phenylosotriazole. The metaperiodate uptake and formaldehyde produced were determined as described above. Table II shows the theoretical and experimental results.

The experimental results show that only the hydroxyl group on position 6 has been substituted thus the periodate oxidation releases carbon 4 as formic acid. This carbon atom of *D*-mannose is difficult to isolate by standard procedure.

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TABLE II								
	Theoretical		Exper	Experimental				
_	10_{4}	НСНО	10,	НСНО				
6-O-Tosyl-D-glucose phenylosotriazole 6-O-Benzoyl-D-glucose phenylosotriazole	2.00 2.00	$0.00 \\ 0.00$	2.05 1.98	$\begin{array}{c} 0.07\\ 0.00 \end{array}$				

EXPERIMENTAL

The 2,4-dinitro-phenylhydrazone of D-xylose was prepared by the method of Lloyd (5) and the mannose phenylhydrazone by the standard method (6).

6-O-Toluene-p-sulphonyl-D-glucose Phenylosotriazole

p-Glucose phenylosotriazole was prepared by the method of Hudson (2). To 0.5 g of the D-glucose phenylosotriazole dissolved in 15 ml of pyridine was added 0.39 g of toluene-p-sulphonyl chloride (1:1.2 mole). The solution was kept overnight at room temperature and was then added to 50 ml of crushed ice. The white precipitate thus produced was collected and the product washed with dilute acetic acid, water, and ethanol. The product was crystallized from ethanol (yield 0.52 g, 70%), m.p. 149-150°. Calc. for C₁₉H₂₁O₆N₃S: C, 54.50%; H, 5.10%. Found: C, 54.54%; H, 5.17%.

6-O-Benzoyl-D-glucose Phenylosotriazole

This was prepared in a manner similar to that of the previous compound. The product was recrystallized from ethanol by the addition of water until the solution became turbid. When the solution was left standing, long, white, needle-shaped crystals were obtained (yield 45%), m.p. 166-167°. Calc. for C₁₉H₁₉O₅N₃: C, 61.70%; H, 5.15%. Found: C, 61.95%; H, 5.39%.

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ELECTRON SPIN RESONANCE ABSORPTION OF BORO-ULTRAMARINE

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The color of ultramarine has been known to be associated with the presence of regulated amounts of alkali and polysulphide sulphur. Gardner and Fraenkel (1) found that ultra-*N.R.C. Postdoctoral Fellow 1957–59. On leave of absence from Department of Chemistry, University of Tokyo, Tokyo, Japan.

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